

2-(1,3-Dithiol-2-ylidene)-1,3-dithiole-4-carbaldehyde

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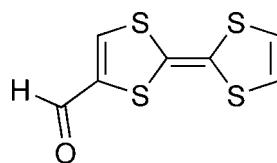
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.024; wR factor = 0.057; data-to-parameter ratio = 25.1.

The structure of the title compound, $\text{C}_7\text{H}_4\text{OS}_4$, at 100 K has orthorhombic symmetry. In the crystal, tetrathiafulvalene molecules form π -stacks along the a axis, with a stacking distance of 3.4736 (6) Å. Along the b axis, parallel stacks are interconnected with each other through a network of weak $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds and short $\text{S}\cdots\text{S}$ contacts [3.4813 (7) Å]. Additional short $\text{S}\cdots\text{S}$ contacts [3.4980 (9) Å] join parallel stacks along the c axis.

Related literature

For tetrathiafulvalene derivatives and their applications, see: Yamada & Sugimoto (2004); Segura & Martín (2001). For a review on synthetic chemistry of tetrathiafulvalenes, see: Fabre (2004). For a previous synthesis of the title compound, see: Garín *et al.* (1994). For reviews on 'weak' non-classical hydrogen bonding, see: Steiner (2002); Desiraju (2005). For reviews on halogen–halogen contacts, see: Metrangolo *et al.* (2008).



Experimental

Crystal data

$\text{C}_7\text{H}_4\text{OS}_4$
 $M_r = 232.34$
Orthorhombic, $P2_12_12_1$
 $a = 3.8466$ (3) Å
 $b = 7.4052$ (7) Å
 $c = 30.577$ (3) Å

$V = 870.99$ (13) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 1.03$ mm⁻¹
 $T = 100$ K
 $0.50 \times 0.21 \times 0.13$ mm

Data collection

Bruker SMART APEX CCD diffractometer

Absorption correction: multi-scan (*SADABS* in *APEX2*; Bruker,

2012)
 $T_{\min} = 0.675$, $T_{\max} = 0.746$
6998 measured reflections

2734 independent reflections
2663 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.015$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.057$
 $S = 1.13$
2734 reflections
109 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.45$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.25$ e Å⁻³
Absolute structure: Flack x determined using 985 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons & Flack, 2004), 1024 Friedel pairs
Flack parameter: 0.01 (4)

Table 1
Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
C1—H1···O1 ⁱ	0.95	2.38	3.228 (3)	149
C3—H3···O1 ⁱ	0.95	2.69	3.445 (3)	137

Symmetry code: (i) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$

Data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINT* (Bruker, 2012); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2013) and *SHELXE* (Hübschle *et al.*, 2011); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010) and *enCIFer* (Allen *et al.*, 2004).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2488).

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supplementary materials

Acta Cryst. (2013). **E69**, o1157 [doi:10.1107/S160053681301711X]

2-(1,3-Dithiol-2-ylidene)-1,3-dithiole-4-carbaldehyde

Matthias Zeller and Vladimir A. Azov

Comment

The title compound, commonly known as 4-formyltetrathiafulvalene, was prepared from tetrathiafulvalene (TTF) and can serve as an intermediate for the synthesis of 4-(hydroxymethyl)tetrathiafulvalene by reduction with NaBH_4 , of conjugated TTF derivatives by means of Wittig reaction (Garín *et al.*, 1994), of TTF imines by reaction with amines, and of other functional tetrathiafulvalenes (Yamada & Sugimoto, 2004; Fabre, 2004).

The molecular structure of the title compound with atom numbering scheme is shown in Fig. 1. Bond lengths and angles may be considered normal. The molecular framework excluding the carbonyl group is essentially planar, with a maximum deviation of fitted atoms from the least-square plane, defined by the heavy atoms of the TTF backbone, of 0.042 (2) Å for C6. Atoms of the carbonyl group show more substantial out of plane deviation of 0.128 (2) Å for C1 and of 0.2393 (19) Å for O1, respectively.

Details of the packing interactions are given in the Tables. Molecules of the 4-formyltetrathiafulvalene form π -stacks along the *a* axis with a distance of 3.4736 (6) Å between the least-square planes defined by the S1, S2, S3, and S4 atoms (Figs. 1 &2). Parallel π -stacks are interconnected with each other along the *b* axis by C1—H1···O1ⁱ and C3—H3···O1ⁱ (symmetry code: (i) $-x, y + 1/2, -z + 1/2$) short contacts, which can be classified as non-classical hydrogen bonds. Additionally, two S···S short contacts, which may be similar in nature to halogen bonds (Metrangolo *et al.*, 2008), are observed in the crystal structure. The shorter S2···S4^{iv} (3.4813 (7) Å) contacts (symmetry code: (iv) $x, 1 + y, z$) are observed along the *b* axis. The longer (3.4980 (9) Å) S3···S3^{ii/iii} contacts (symmetry codes: (ii) $-1/2 + x, 1/2 - y, -z$; (iii) $1/2 + x, 1/2 - y, -z$) bind parallel π -stacks with each other along the *c* axis.

Experimental

The title compound was prepared as described by Garín *et al.* (1994) by treatment of monolithio-TTF with *N*-methyl-*N*-phenylformamide in dry Et_2O . The product was obtained as a deep red microcrystalline solid. Crystals suitable for X-ray diffraction were grown by slow evaporation of a solution in benzene/cyclohexane. Mp: 382–383 K; Lit: 382–383 K (Garín *et al.*, 1994). ^1H NMR (200 MHz, CDCl_3): δ 6.33 (d, $J = 6.5$ Hz, 1 H), 6.36 (d, $J = 6.2$ Hz, 1 H), 7.42 (s, 1 H), 9.48 (s, 1 H).

Refinement

Hydrogen atoms were included at calculated positions using a riding model with aromatic and formyl C—H = 0.95. The $U_{\text{iso}}(\text{H})$ values were fixed at $1.2 \times U_{\text{eq}}(\text{C})$ of the parent C atom.

Computing details

Data collection: *APEX2* (Bruker, 2012); cell refinement: *APEX2* (Bruker, 2012); data reduction: *APEX2* (Bruker, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2013) and *SHELXLE* (Hübschle *et al.*, 2011); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012)

and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010) and *enCIFer* (Allen *et al.*, 2004).

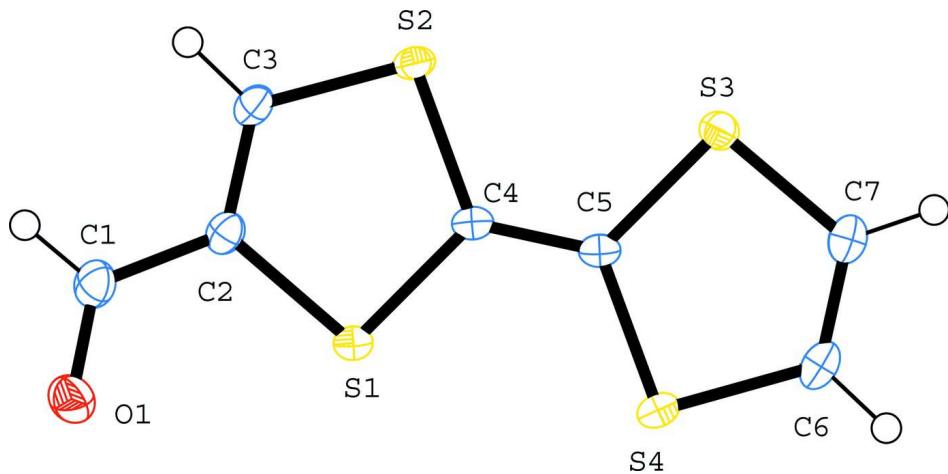


Figure 1

ORTEP-3 plot of the title molecule with the atom numbering scheme. Displacement ellipsoids are represented at 50% probability levels. H atoms are presented as a small spheres of arbitrary radius.

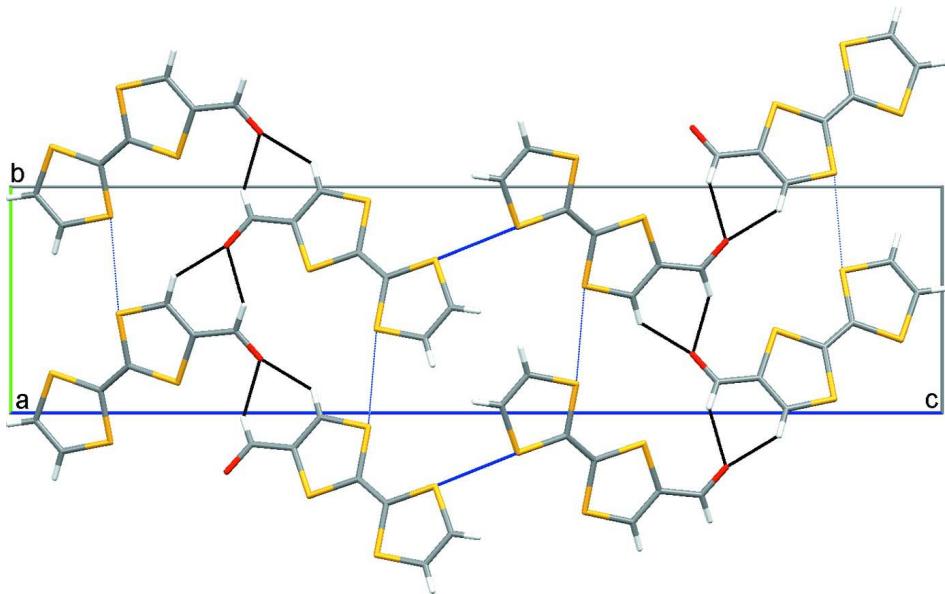
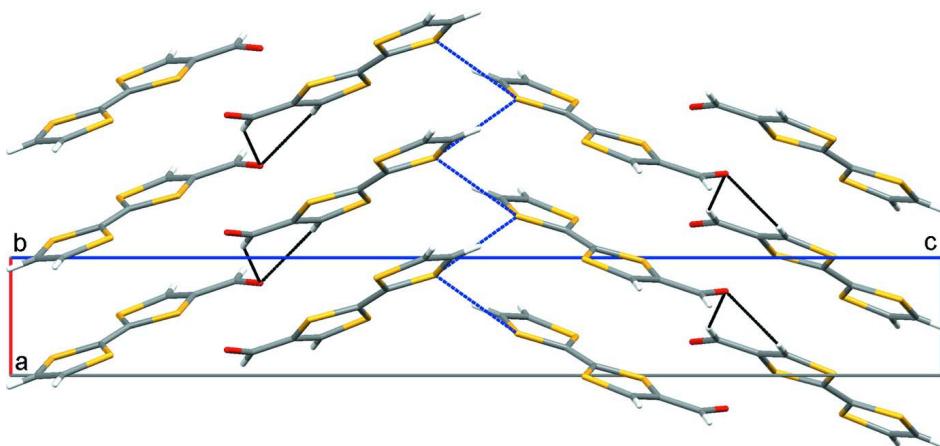


Figure 2

Crystal packing of the title compound viewed along the a axis. Hydrogen bonds are shown as solid black lines, short S3···S3 contacts are shown as solid blue lines, and short S2···S4 contacts are represented as dotted blue lines.

**Figure 3**

Crystal packing of the title compound viewed along the *b* axis. Hydrogen bonds are shown as solid black lines, short S3...S3 contacts are shown as solid blue lines.

2-(1,3-Dithiol-2-ylidene)-1,3-dithiole-4-carbaldehyde

Crystal data

C₇H₄OS₄
 $M_r = 232.34$
Orthorhombic, $P2_12_12_1$
 $a = 3.8466 (3) \text{ \AA}$
 $b = 7.4052 (7) \text{ \AA}$
 $c = 30.577 (3) \text{ \AA}$
 $V = 870.99 (13) \text{ \AA}^3$
 $Z = 4$
 $F(000) = 472$

$D_x = 1.772 \text{ Mg m}^{-3}$
Melting point: 383 K
Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Cell parameters from 4789 reflections
 $\theta = 2.8\text{--}31.4^\circ$
 $\mu = 1.03 \text{ mm}^{-1}$
 $T = 100 \text{ K}$
Plate, red
 $0.50 \times 0.21 \times 0.13 \text{ mm}$

Data collection

Bruker SMART APEX CCD
diffractometer
Radiation source: fine focus sealed tube
 ω and φ scans
Absorption correction: multi-scan
(*SADABS* in *APEX2*; Bruker, 2012)
 $T_{\min} = 0.675$, $T_{\max} = 0.746$
6998 measured reflections

2734 independent reflections
2663 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.015$
 $\theta_{\max} = 31.9^\circ$, $\theta_{\min} = 1.3^\circ$
 $h = -5 \rightarrow 5$
 $k = -10 \rightarrow 10$
 $l = -42 \rightarrow 44$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.057$
 $S = 1.13$
2734 reflections
109 parameters
0 restraints
Primary atom site location: structure-invariant
direct methods
Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites
H-atom parameters constrained
 $w = 1/[s^2(F_o^2) + (0.0237P)^2 + 0.4121P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.45 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.25 \text{ e \AA}^{-3}$
Absolute structure: Flack x determined using
985 quotients $[(I+)-(I-)]/[(I+)+(I-)]$ (Parsons &
Flack, 2004), 1024 Friedel pairs.
Flack parameter: 0.01 (4)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.1960 (6)	0.3626 (3)	0.24133 (7)	0.0229 (4)
H1	0.0987	0.4745	0.2504	0.027*
C2	0.3148 (6)	0.3446 (3)	0.19636 (7)	0.0178 (4)
C3	0.3234 (6)	0.4823 (3)	0.16743 (7)	0.0188 (4)
H3	0.2417	0.5992	0.1751	0.023*
C4	0.5823 (5)	0.2086 (3)	0.12667 (7)	0.0154 (4)
C5	0.7332 (5)	0.1004 (3)	0.09665 (7)	0.0154 (4)
C6	0.9971 (6)	-0.1700 (3)	0.05523 (7)	0.0213 (4)
H6	1.0784	-0.2866	0.0473	0.026*
C7	1.0078 (7)	-0.0331 (3)	0.02682 (7)	0.0213 (4)
H7	1.0959	-0.0492	-0.0019	0.026*
O1	0.2158 (5)	0.2405 (2)	0.26790 (5)	0.0275 (4)
S1	0.47171 (14)	0.13395 (6)	0.17941 (2)	0.01732 (10)
S2	0.48840 (15)	0.43791 (6)	0.11609 (2)	0.01750 (10)
S3	0.85438 (14)	0.17653 (7)	0.04434 (2)	0.01774 (11)
S4	0.82962 (14)	-0.12822 (7)	0.10718 (2)	0.01786 (11)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0258 (11)	0.0227 (9)	0.0202 (10)	0.0009 (9)	-0.0027 (8)	-0.0048 (8)
C2	0.0168 (9)	0.0174 (9)	0.0190 (9)	0.0009 (8)	-0.0026 (7)	-0.0033 (7)
C3	0.0204 (10)	0.0154 (8)	0.0206 (10)	0.0022 (8)	-0.0014 (9)	-0.0033 (7)
C4	0.0151 (9)	0.0134 (8)	0.0177 (9)	-0.0006 (6)	-0.0023 (7)	0.0024 (6)
C5	0.0150 (9)	0.0132 (8)	0.0180 (9)	-0.0011 (6)	-0.0020 (7)	0.0027 (7)
C6	0.0193 (9)	0.0186 (9)	0.0260 (10)	0.0023 (9)	-0.0008 (9)	-0.0069 (7)
C7	0.0201 (10)	0.0217 (9)	0.0221 (10)	0.0006 (9)	0.0005 (9)	-0.0056 (7)
O1	0.0359 (10)	0.0274 (8)	0.0192 (7)	-0.0016 (8)	-0.0012 (7)	-0.0002 (6)
S1	0.0208 (2)	0.01368 (19)	0.0175 (2)	0.00034 (19)	0.00125 (19)	0.00193 (17)
S2	0.0205 (2)	0.01230 (18)	0.0197 (2)	0.00120 (19)	-0.0006 (2)	0.00242 (16)
S3	0.0183 (2)	0.0181 (2)	0.0169 (2)	0.00035 (19)	0.00033 (19)	0.00149 (17)
S4	0.0192 (2)	0.01267 (19)	0.0217 (2)	0.00182 (19)	-0.00120 (19)	0.00094 (17)

Geometric parameters (\AA , $^{\circ}$)

C1—O1	1.218 (3)	C4—S2	1.7661 (19)
C1—C2	1.455 (3)	C5—S3	1.759 (2)
C1—H1	0.9500	C5—S4	1.763 (2)
C2—C3	1.350 (3)	C6—C7	1.336 (3)
C2—S1	1.751 (2)	C6—S4	1.742 (2)
C3—S2	1.725 (2)	C6—H6	0.9500

C3—H3	0.9500	C7—S3	1.745 (2)
C4—C5	1.349 (3)	C7—H7	0.9500
C4—S1	1.757 (2)		
O1—C1—C2	122.9 (2)	C4—C5—S4	122.44 (15)
O1—C1—H1	118.6	S3—C5—S4	114.71 (12)
C2—C1—H1	118.6	C7—C6—S4	118.03 (16)
C3—C2—C1	123.9 (2)	C7—C6—H6	121.0
C3—C2—S1	118.05 (16)	S4—C6—H6	121.0
C1—C2—S1	118.02 (16)	C6—C7—S3	117.70 (17)
C2—C3—S2	117.48 (16)	C6—C7—H7	121.1
C2—C3—H3	121.3	S3—C7—H7	121.1
S2—C3—H3	121.3	C2—S1—C4	94.30 (10)
C5—C4—S1	122.80 (15)	C3—S2—C4	95.26 (10)
C5—C4—S2	122.29 (15)	C7—S3—C5	94.82 (10)
S1—C4—S2	114.90 (11)	C6—S4—C5	94.69 (10)
C4—C5—S3	122.85 (15)		
O1—C1—C2—C3	-174.0 (2)	C5—C4—S1—C2	178.23 (18)
O1—C1—C2—S1	3.4 (3)	S2—C4—S1—C2	-0.66 (13)
C1—C2—C3—S2	177.51 (17)	C2—C3—S2—C4	-0.5 (2)
S1—C2—C3—S2	0.1 (3)	C5—C4—S2—C3	-178.19 (18)
S1—C4—C5—S3	-178.29 (12)	S1—C4—S2—C3	0.71 (13)
S2—C4—C5—S3	0.5 (3)	C6—C7—S3—C5	-1.6 (2)
S1—C4—C5—S4	0.8 (3)	C4—C5—S3—C7	-178.51 (18)
S2—C4—C5—S4	179.63 (12)	S4—C5—S3—C7	2.32 (14)
S4—C6—C7—S3	0.3 (3)	C7—C6—S4—C5	1.2 (2)
C3—C2—S1—C4	0.3 (2)	C4—C5—S4—C6	178.61 (18)
C1—C2—S1—C4	-177.22 (18)	S3—C5—S4—C6	-2.21 (14)

Hydrogen-bond geometry (\AA , $^\circ$)

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
C1—H1 \cdots O1 ⁱ	0.95	2.38	3.228 (3)	149
C3—H3 \cdots O1 ⁱ	0.95	2.69	3.445 (3)	137

Symmetry code: (i) $-x, y+1/2, -z+1/2$.Sulfur-sulfur short contacts (\AA) of the title compound

System S \cdots S	S \cdots S	Symmetry code
S3 \cdots S3 ⁱⁱ	3.4980 (9)	(ii) $-1/2+x, 1/2-y, -z$
S3 \cdots S3 ⁱⁱⁱ	3.4980 (9)	(iii) $1/2+x, 1/2-y, -z$
S2 \cdots S4 ^{iv}	3.4813 (7)	(iv) $x, 1+y, z$